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Ground-state properties of ordered, partially ordered, and random Cu-Au and Ni-Pt alloys

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We have studied the ground-state properties of ordered, partially ordered, and random Cu-Au and Ni-Pt alloys at the stoichiometric $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ compositions in the framework of the multisublattice single-site (SS) coherent potential approximation (CPA). Charge-transfer effects in the random and the partially ordered alloys are included in the screened impurity model. The prefactor in the Madelung energy is determined by the requirement that the total energy obtained in direct SS CPA calculations should equal the total energy given by the Connolly-Williams expansion based on Green's function calculations for the ordered alloys that do not rely on the single-site approximation. We find that the prefactor to a large degree is independent of lattice constant, concentration, and the long-range-order parameter and may be considered constant for a given alloy system. The calculated heats of formation for the ordered alloys are in good agreement with experimental data. For all the alloys the calculated ordering energy and the equilibrium lattices parameters are found to be almost exact quadratic functions of the long-range-order parameter.

I. INTRODUCTION

In recent years there have appeared a number of first-principles theoretical investigations of ordering phenomena in Cu-Au (Refs. 1–12) and Ni-Pt (Refs. 12–15) alloys and of the influence of ordering effects on their electronic structure and thermodynamic properties. In all these investigations, except in the work by Kudrnovsky *et al.*,⁸ who calculated the electronic structure of partially ordered Cu₃Au alloys, one considers only two states of the alloys, i.e., completely random or completely ordered. Nevertheless, there exists an intermediate, partially ordered state that is a consequence of atomic rearrangements between the sublattices of the ordered alloy and, to a certain extent, preserves the difference between sublattice sites. In fact, under normal experimental circumstances it is difficult to avoid the partially ordered state because of thermal fluctuations and deviations from exact stoichiometric compositions during the alloy preparation.

At the present time it is generally accepted that traditional energy band-structure methods based on density-functional theory give a reliable quantitative description of the electronic structure and ground-state properties of completely ordered crystalline solids. Moreover, it has recently become clear that this approach may also be used in calculations of thermodynamic properties including phase diagrams of partially ordered or random al-

loys if applied in conjunction with the Connolly-Williams method (CWM),¹⁶ the special quasirandom structure,¹⁷ or related methods.⁴ However, these methods are based on expansions of the total energy in some parameters and are restricted to systems where the underlying electronic structure changes smoothly, e.g., as a function of concentration. An alternative approach based on direct calculations of the electronic structure of random or partially ordered alloys at a given composition and order is the single-site (SS) coherent potential approximation (CPA), which has proven to be most accurate and reliable.¹⁸

Recent applications^{11,19–29} show that the SS CPA yields equilibrium lattice parameters, bulk moduli, and enthalpies of formation with an accuracy similar to that obtained by ordinary first-principles methods for ordered solids. However, in comparison to the latter methods the SS CPA includes one additional approximation, i.e., the single-site approximation, and at present it is still unknown to what extent this additional approximation influences the accuracy of the calculated electronic and ground-state properties. It appears that the most important source of error is the uncertainty in the treatment of charge-transfer effects, e.g., through the definition of a Madelung potential of the alloy components and a corresponding Madelung energy.²⁹

There exists a number of models that treat charge transfer effects in random metallic alloys^{9,30} including models based on the SS CPA.^{19,21,22,26} These models were re-

cently discussed by Korzhavyi *et al.*,³¹ who found that the Madelung energy in all cases had the same mathematical form but with a different prefactor. It was also found that no single value of this prefactor would lead to perfect agreement between theory and experiment. To solve this problem, it was suggested that one might choose the Madelung prefactor in such a way that the total energy of a completely random alloy obtained in direct SS CPA calculations should equal the total energy of the same system, but obtained by a Connolly-Williams expansion based on Green's function calculations for the ordered alloys, which in this context may be considered exact as far as treatment of charge transfer effects is concerned. In the present paper we shall exploit this approach further.

II. METHOD OF CALCULATION

The generalization of the usual SS CPA to solids with several different sublattices is straightforward^{8,24,32,33} and below we therefore present only a brief outline of the technique.

A. Multisublattice LMTO CPA method

Let us consider an ordering A_cB_{1-c} alloy, where c is the concentration of the A species, with k α -type sublattices and m β -type sublattices. In the completely ordered state the alloy therefore has the formula A_kB_m . For simplicity we assume that all the α as well as all the β sublattices are equivalent. To describe a partially ordered state of such an alloy it is sufficient to introduce a single long-range-order (LRO) parameter η . If we call the concentration of the A species on the α and β sublattices c_α and c_β , respectively, η may be defined as

$$\eta = c_\alpha - c_\beta. \quad (1)$$

In turn, c_α and c_β may be expressed in terms of η and the concentration c as

$$c_\alpha = c + \frac{m}{n}\eta, \quad c_\beta = c - \frac{k}{n}\eta, \quad (2)$$

where $n = k + m$ is the total number of sublattices in the alloy.

In any partially ordered alloy there exist also short-range-order (SRO) effects. However, in the framework of the single-site approximation it is possible to take into account only those SRO effects, which are caused directly by the long-range order. Furthermore, each sublattice is considered a completely random alloy with corresponding concentrations of A and B species. Thus, in the single-site approximation the partially ordered alloy is viewed as a set of coexisting completely random alloys.

The key self-averaging quantity, which should be determined in order to calculate the electronic structure and ground-state properties of an alloy, is the average one-electron Green's function of the system. To obtain this quantity we apply the SS CPA in conjunction with the linear muffin-tin orbitals (LMTO) method in the

atomic sphere approximation (ASA). Hereby the average one-electron Green's function may be obtained in the form of the Korringa-Kohn-Rostoker (KKR) ASA Green's function,³⁴ which is analogous to the scattering path operator in multiple scattering theory. For a complex energy z we have

$$\tilde{g}_{ij}(z) = \frac{1}{V_{\text{BZ}}} \int_{\text{BZ}} d^3k [\tilde{P}(z) - S(\mathbf{k})]^{-1}_{ij}, \quad (3)$$

where V_{BZ} is the volume of the Brillouin zone (BZ), $S(\mathbf{k})$ the LMTO structure constants, and $\tilde{P}(z)$ the crystal coherent-potential-function matrix. In the expression the subscripts i and j refer to individual sublattice sites in the unit cell and the tilde labels average (coherent potential) quantities. Finally, we have suppressed the angular momentum quantum numbers (lm) as well as the LMTO representation label. The coherent-potential-function matrix that enters (3) is block diagonal

$$\tilde{P} = \begin{pmatrix} \tilde{P}_1 & 0 & \dots & 0 \\ 0 & \tilde{P}_2 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \tilde{P}_n \end{pmatrix} \quad (4)$$

and each diagonal element \tilde{P}_i is the coherent-potential function of the i sublattice. To obtain the complete coherent-potential-function matrix in the single-site approximation one must, for each of the n sublattices, solve an equation of the form

$$\tilde{P}_i = c_i P_i^A + (1 - c_i) P_i^B + [P_i^A - \tilde{P}_i] \tilde{g}_{ii} [P_i^B - \tilde{P}_i], \quad (5)$$

where c_i is the concentration of A atoms and P_i^κ the potential function of the κ species on sublattice i . In the α representation of the LMTO method the potential function may be parametrized in the form³⁵

$$P_{il}^{\alpha\kappa}(z) = \frac{C_{il}^\kappa - z}{(C_{il}^\kappa - z)(\gamma_{il}^\kappa - \alpha_l) + \Delta_{il}^\kappa} \quad (6)$$

in terms of the center C , bandwidth Δ , and γ potential parameters obtained from the solution of the radial Schrödinger equation at a particular energy E_ν and angular momentum l .

Although it might appear so, the coherent-potential functions on different sublattices are not independent. In fact, they are coupled by the definition \tilde{g} (3) of the coherent Green's function, which, together with (5), form the nonlinear system of CPA equations, which must be solved self-consistently.

B. Madelung potential and energy

When the system of CPA equations is solved, one may calculate the valence charge density ρ_i^κ of the atomic species κ in the sphere at the i sublattice.⁷ Related to the charge density is the net charge on site i , which in the ASA is

$$Q_i^\kappa = Z_{\text{val}}^\kappa - \int_{S_i} d^3r \rho_i^\kappa, \quad (7)$$

where the integral is taken over the atomic sphere of radius S_i and Z_{val}^κ is the number of the valence electrons of the κ atom.

Connected with the net charge is the Madelung potential of atom κ on sublattice i . In the mean-field approximation, where configurational correlations are neglected, this Madelung potential only depends on the sublattice. It has the form

$$V_i^0 = \frac{e^2}{S} \sum_j M_{ij} \tilde{Q}_j, \quad (8)$$

where M_{ij} is the Madelung matrix of the crystal lattice, S the average atomic Wigner-Seitz radius of the alloy, and \tilde{Q}_i the average net charge on sublattice i

$$\tilde{Q}_i = c_i Q_i^A + (1 - c_i) Q_i^B. \quad (9)$$

To solve the SS CPA equations one needs at each iteration the one-electron potential for each atomic species at each sublattice. It is therefore necessary to consider a single atom embedded in an effective medium where the average charges on the sublattices obey the condition of charge neutrality

$$\sum_i \tilde{Q}_i = 0. \quad (10)$$

It follows that if the κ atom on the i sublattice has a net charge different from the average value \tilde{Q}_i , the complete system, i.e., the atom plus the effective medium, will have an extra charge $Q_i^\kappa - \tilde{Q}_i$, which must be compensated in some way to keep the system neutral.

Recent Green's function calculations of impurity atoms in metals³⁶ show that almost all of the compensating charge is located in the first coordination shell around the impurity. This observation is the basis of the screened impurity model (SIM),^{22,29,31} according to which each atom κ on the sublattice i has an additional Madelung potential

$$V_{i\kappa}^1 = e^2 \frac{Q_i^\kappa - \tilde{Q}_i}{R_1}, \quad (11)$$

caused by the compensating charge located in the first coordination shell of radius R_1 . The complete Madelung potential of each alloy species is therefore

$$V_{i\kappa}^M = V_i^0 + V_{i\kappa}^1. \quad (12)$$

Related to the Madelung potential there will be a corresponding Madelung energy consisting of two terms

$$E_M = E_M^0 + E_M^1, \quad (13)$$

where the first is the ordinary Madelung energy of the electrostatic interaction of the effective sublattices

$$E_M^0 = \frac{e^2}{2S} \sum_{i,j} M_{ij} \tilde{Q}_i \tilde{Q}_j \quad (14)$$

and the second is the energy associated with the compen-

sating charges. In Ref. 31 it was shown that this latter term may be written

$$\begin{aligned} E_M^1 &= -\beta \frac{e^2}{nR_1} \sum_i [c_i (Q_i^A - \tilde{Q}_i)^2 + (1 - c_i) (Q_i^B - \tilde{Q}_i)^2] \\ &= -\beta \frac{e^2}{nR_1} \sum_i c_i (1 - c_i) (Q_i^A - Q_i^B)^2, \end{aligned} \quad (15)$$

where β is a prefactor that depends on the particular model used to describe the charge transfer effects. For example, in the screened CPA method²⁶ $\beta = 0.5$, in the charge-correlated model,⁹ $\beta \sim 0.6 - 0.7$, and in the SIM, $\beta = 1$ when the interaction between the screening charges themselves is neglected.

C. Determination of β

Korzhavii *et al.*³¹ tested different values of the prefactor β in a number of alloys exhibiting considerable charge-transfer effects and found that no single value, e.g., $\beta = 1$ or $\beta = 0.5$, worked in all the systems considered. It was therefore suggested that β may be regarded as a constant only for a given system and crystal structure and that its value may be determined on the basis of data obtained beyond the single-site approximation. For instance, a possible value of β may be found by comparing calculated and measured properties such as lattice constants and heats of formation. However, in such a comparison one should realize that real, random alloys differ from the ideal systems considered in SS CPA calculations by possible SRO effects as well as local distortions of the lattice caused by the difference in the atomic sizes of the alloy species. In fact, this appears to be the case for the Cu-Au and Ni-Pt random alloys,^{4,10,12,15} which we are considering here.

A more consistent solution to the problem of finding a system-dependent optimal value of β may be based on the results from first-principles methods for ordered alloys, which in the present context treat charge-transfer effects and electrostatic energies exactly. In this case the lattice constants as well as the total and mixing energies of completely random alloys may be obtained by means of the Connolly-Williams method¹⁶ through the calculation of the cluster interactions parameters. Thus one may find a value for β by comparing SS CPA calculations including (13) with results from CWM calculations. Alternatively, since the cluster interaction parameters may be obtained also from SS CPA calculations one may find a prefactor β , which makes the two sets of cluster interaction parameters (CWM and SS CPA) agree to some accuracy.

It is not obvious that such a procedure should work in all cases because in general one would expect some dependence of the prefactor on the value of the lattice parameter, the alloy composition, and even on the LRO parameter. However, as we shall show, one may, at least in the alloy systems considered here, neglect these dependences and for each alloy system choose a single value of β that allows one to reproduce with acceptable accuracy

thermodynamic properties in a broad range of these external parameters.

D. Connolly-Williams method for partially ordered and random alloys

The Connolly-Williams method¹⁶ is based on a phenomenological expansion of the total energy of a given alloy in terms of atomic distribution correlation functions $\langle \sigma_{i\alpha} \sigma_{j\beta} \cdots \sigma_{k\gamma} \rangle$, which are the averages of the products of spinlike variables $\sigma_{i\alpha}$ taking on values $+1$ or -1 , depending on whether the α site of the i sublattice is occupied by A or B atoms, respectively. The total energy of an alloy is expressed as

$$E = \sum_n v_n \xi_n, \quad (16)$$

where the sum runs over clusters of different types, v_n is a cluster interaction parameter for a particular cluster, and ξ_n is the corresponding spin product.

The basic idea of the Connolly-Williams method is to calculate the total energy of a number of different supercells for a given lattice and then solve the corresponding number of equations of the form (16) for the cluster interactions v_n . There are many ways to determine a set of cluster interactions (see, for example, Ref. 37), but for our purpose, i.e., the comparison of the energetics obtained on the basis of total energy calculations for ordered alloys with CPA results, we calculate the so-called unrelaxed cluster interactions,³⁷ which completely neglect lattice relaxation effects caused by differences in the atomic sizes of the alloy components. This means that the set of total energies used to solve (16) must be calculated at the same volume and hence the unrelaxed cluster interactions are volume dependent. Note that the unrelaxed cluster interactions in fact fail to give a correct description of the Cu-Au and Ni-Pt phase diagrams because lattice relaxation effects are important in these two systems.^{4,15} However, we use the cluster interactions only to determine the prefactor β in (15), and after a value is found any other type of cluster interactions may be obtained and used in, say, the calculation of the phase diagram.

In the present calculations we find that the expansion in the unrelaxed cluster interactions is rapidly convergent and that we need only keep the five terms in (16) that correspond to the four-site interactions of the tetrahedra of the nearest neighbors in the fcc lattice. Therefore, we consider in the supercell calculations for the completely ordered alloys the pure A and B elements in the fcc structure, the AB compound in the $L1_0$ structure, and the A_3B and AB_3 compounds in the $L1_2$ structure.

In the case of the partially ordered alloys we have used the total energy of partially ordered A_3B ($L1_2$), AB ($L1_0$), and AB_3 ($L1_2$) alloys as defined in the mean-field approximation, i.e., without SRO effects on the alloy sublattices as required by the CPA. The total energies in the three cases are

$$\begin{aligned} E_{A_3B} &= v_0 + v_1\sigma + v_2(\sigma^2 - \frac{1}{4}\eta^2) + v_3(\sigma^3 - \frac{3}{4}\sigma\eta^2 + \frac{1}{4}\eta^3) \\ &\quad + v_4(\sigma^4 - \frac{3}{2}\sigma^2\eta^2 + \sigma\eta^3 - \frac{3}{16}\eta^4), \\ E_{AB} &= v_0 + v_1\sigma + v_2(\sigma^2 - \frac{1}{3}\eta^2) \\ &\quad + v_3\sigma(\sigma^2 - \eta^2) + v_4(\sigma^2 - \eta^2)^2, \\ E_{AB_3} &= v_0 + v_1\sigma + v_2(\sigma^2 - \frac{1}{4}\eta^2) + v_3(\sigma^3 - \frac{3}{4}\sigma\eta^2 - \frac{1}{4}\eta^3) \\ &\quad + v_4(\sigma^4 - \frac{3}{2}\sigma^2\eta^2 - \sigma\eta^3 - \frac{3}{16}\eta^4), \end{aligned} \quad (17)$$

where $\sigma = 2c - 1$ is the average spin variable of the alloy of concentration c and η the long-range-order parameter defined in Sec. II A. For a completely random state $\eta = 0$ and for this value, the three expressions (17) become equivalent and equal to the energy of a random alloy

$$E_{\text{rand}} = v_0 + v_1\sigma + v_2\sigma^2 + v_3\sigma^3 + v_4\sigma^4. \quad (18)$$

In the present work Eqs. (17) and (18) have been used to calculate the ground-state properties of random and partially ordered alloys based on the cluster interaction parameters obtained from ordered alloys by the CWM. In addition, they have been used to determine the cluster interactions of random and partially ordered alloys from total energies obtained in CPA calculations. In the case of a random alloy the cluster interactions were obtained on the basis of the total energy of the pure elements as well as completely random alloys at different concentrations, while in the case of a partially ordered alloy the cluster interactions were obtained from the total energies of a single alloy structure at a fixed concentration but with different values of the LRO parameter η .

E. Details of calculation

All the calculations for partially ordered and random alloys have been performed in the scalar-relativistic approximation and the ASA by means of the LMTO CPA method^{7,24} in the tight-binding representation.^{35,38,39} For the pure elements and the ordered compounds we have used the LMTO Green's function (GF) technique instead of solving the conventional Hamiltonian eigenvalue problem. Thereby we treat these systems numerically on the same footing as the random alloys. This allows us to compare directly the calculated electronic structure and ground-state properties of random and ordered alloys. In the latter case we have also found that the difference between the results of the LMTO GF calculations and the second-order tight-binding LMTO Hamiltonian calculations is practically negligible. For example, the difference in the total energy of Cu_3Au is about 0.03 mRy/atom.

Only valence electrons with $l_{\text{max}} = 2$ were treated self-consistently in the local-density approximation (LDA) with the Perdew-Zunger parametrization⁴⁰ of the results of Ceperley and Alder⁴¹ for the exchange-correlation potential and energy. Core electrons were frozen after initial atomic calculations. We have tested the influence of this so-called frozen-core approximation³⁴ on the calculated ground-state properties and found that it may safely be used, at least in the calculations for the present systems. For instance, the difference between the results of all-electron and frozen-core calculations is less than 1% for

the equilibrium lattice parameter and 10% for the bulk modulus, i.e., within the accepted range of errors in the LDA and the ASA. Moreover, as expected, it becomes negligible in the comparison of ground-state properties of ordered and disordered states.

All alloy and pure metal calculations have been performed in a simple cubic structure with four sublattice sites corresponding to the fcc structure with lattice parameter a , i.e., $(0, 0, 0)$, $\frac{a}{2}(1, 1, 0)$, $\frac{a}{2}(1, 0, 1)$, and $(0, 1, 1)\frac{a}{2}$, where the probability of occupation by different atoms depends on the composition, stoichiometric formula, and the value of the LRO parameter η . For pure metals and random alloys all four sublattices are equivalent, while for the Cu_3Au , Au_3Cu , Ni_3Pt , and Pt_3Ni completely and partially ordered alloys in the L_{12} structure three sublattices are equivalent and different from the fourth and for the CuAu and NiPt ordered alloys in the L_{10} structure with a c/a ratio equal to 1 there are two sets of equivalent sublattices.

The integration over the Brillouin zone (3) has been performed by the special point technique. For pure metals, random alloys, and the L_{12} ordered alloys we used 56 \mathbf{k} points in the irreducible wedge (1/48) of the simple cubic Brillouin zone and for the L_{10} alloys we used 168 \mathbf{k} points in the irreducible wedge (1/16) of the Brillouin zone, of the simple tetragonal lattice. In order to calculate integrals over the whole Brillouin zone, which is needed for the off-diagonal elements of the Green's function \tilde{g} , which enters the CPA equation (5), we applied the 48 proper symmetry operations of the L_{12} structure and the 16 symmetry operations of the L_{10} structure to each \mathbf{k} point in the irreducible Brillouin zone wedge, i.e.,

$$\tilde{g} = \frac{1}{V_{\text{BZ}}} \int_{\text{IBZ}} d\mathbf{k} \sum_T U(T) [\tilde{\mathbf{P}} - \mathbf{S}(\mathbf{k})]^{-1} U(T)^{-1}, \quad (19)$$

where $U(T)$ is the unitary transformation matrix, which transforms the KKR ASA Green's function $[\tilde{\mathbf{P}} - \mathbf{S}(\mathbf{k})]^{-1}$ under the symmetry operation T . For completely random alloys where all the sublattices are equivalent and have cubic symmetry, \tilde{g} is diagonal in the cubic harmonic representation with $l_{\text{max}} = 2$. The time-consuming summation over T in (19) may in that case be performed analytically by means of the orthogonality relations.²⁴ For completely ordered alloys no summation over T is needed because only the trace of the Green's function averaged over equivalent sublattice sites enters the problem and this is invariant under the symmetry transformations (19).

In all the calculations the individual atomic sphere radii were set equal to the radius of the average atomic Wigner-Sietz sphere of the alloy. The moments of the state density needed for the kinetic energy and the valence charge density were calculated by integrating the Green's function on a complex energy contour using a Gaussian integration technique with 16 points on a semi-circle enclosing the occupied states. The convergence criteria for the total energy was 0.001 mRy. The equilibrium lattice parameter and corresponding ground-state energy of a given alloy were obtained on the basis of five self-consistent calculations of the total energy close to the

equilibrium lattice parameter and a subsequent fit to a Morse-type equation of state.⁴²

III. OPTIMAL β VALUE

According to the procedure outlined in Sec. II C, one may obtain an optimal value for the SIM Madelung parameter β by a comparison between CWM and CPA total energy calculations for random alloys. In Fig. 1 we present such a comparison for the Cu-Au system and from the figure one may observe that the results of CPA calculations with $\beta = 0.74$ are identical to those obtained by the CWM, at all concentrations. A similar comparison for the Ni-Pt system leads to an optimal value of $\beta = 0.6$ and we conclude that β may be considered constant for

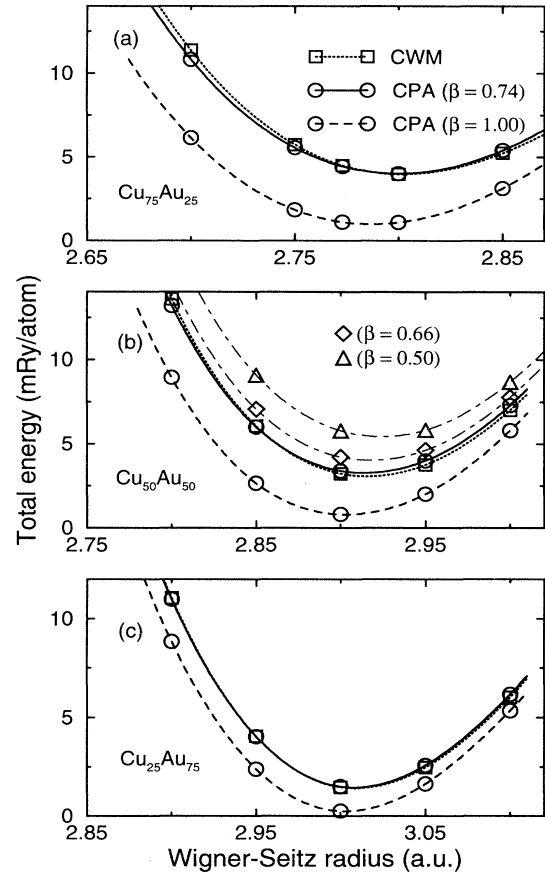


FIG. 1. Comparison between calculated binding energies for (a) $\text{Cu}_{75}\text{Au}_{25}$, (b) $\text{Cu}_{50}\text{Au}_{50}$, and (c) $\text{Cu}_{25}\text{Au}_{75}$ random alloys relative to the energy of the standard state $E^0 = cE_{\text{Cu}}^0 + (1-c)E_{\text{Au}}^0$, where c is the Cu concentration and E_{Cu}^0 and E_{Au}^0 the equilibrium energies of Cu and Au, respectively. The results have been obtained by the expansion (18) with cluster-interaction parameters derived by the Connolly-Williams method on the basis of total energies of ordered alloys and by the LMTO CPA method in the SIM with several choices for β . In (b) $\beta = 0.50$ corresponds to the screened CPA method (Ref. 26) and $\beta = 0.66$ to the charge-correlated model (Ref. 9).

a given alloy system independent of concentration, LRO, and lattice spacing. It should be pointed out, however, that we find that β may depend on the crystal structure, e.g., for fcc Ni-Al alloys $\beta = 0.6$ while for bcc Ni-Al alloys $\beta = 0.96$.

Based on the present experience as well as previous calculations,³¹ one may expect that ground-state properties of random alloys may be calculated by the SS CPA with an accuracy similar to the one found in calculations for ordered alloys. However, to obtain such an accuracy one must take account of charge transfer effects, for instance, in the form outlined above. The expectation that a universal value of β would lead to the required accuracy in all alloy systems is not substantiated and instead we find that the optimal value varies in the range from 0.5 to 1. On the other hand, judging from Fig. 1(b) both the screened CPA method²⁶ corresponding to $\beta = 0.5$ and the charge-correlated model⁹ corresponding to $\beta = 0.66$ would do much better for the Cu-Au system than the conventional complete neglect of charge transfer effects.

A. Cluster interactions: Dependence on β

As an alternative to the comparison of binding energies one may consider the calculated cluster-interaction parameters v_n of the expansion (16). Note that since v_0 and v_1 define the standard state from which relative energy changes are measured, only the higher-order terms will be important. In Table I we therefore present selected sets of the calculated volume-dependent unrelaxed cluster interactions v_2 , v_3 , and v_4 for the CuAu and NiPt systems which correspond to a termination of the series at four-site interactions, i.e., at the tetrahedron of nearest neighbors. For the ordered phases the cluster interactions are based on total energy calculations for the two pure components and the three ordered phases A_3B , AB , and AB_3 . For the completely random alloys the cluster interactions are based on the total energies of the two pure components and three random alloys at concentrations of 25, 50, and 75 at.%. Finally, for the partially ordered alloys the cluster interactions are based on the total energies of the two pure components and of partially random alloys at fixed concentrations but with three different values of the LRO parameter $\eta = 0.0, 0.5$, and 0.8 . In the case of equiatomic, partially random alloys, i.e., CuAu and NiPt, we did not extract cluster interactions because in this case E_{AB} of Eq. (17) is a function of η^2 and η^4 only.

To form a useful expansion of the total energy of an alloy as a function of concentration and order one must require that the cluster-interaction parameters are independent of the configurations used in the first-principles calculations from which they are extracted. Ideally, it should therefore be possible to select a value of β such that the cluster interactions derived from CPA calculations for random configurations agree with those obtained from calculations for the ordered alloys. In practice one must expect some dependence on the configurations of the underlying first-principles calculations, e.g., because in a fit to the truncated expansion (16)

the higher-order interactions that are neglected will be redistributed over the calculated cluster interactions depending on the configurational parameters. Hence, even if the calculated total energies of the alloys were exact the extracted cluster interactions would still be somewhat different.

From Table I one observes that the extracted cluster interactions for the ordered alloys satisfy the conditions $v_2 \gg v_3 \gg v_4$, which indicate that the expansion (16), at least for CuAu and NiPt alloys, may be truncated at $n = 4$. One also observes that the cluster interactions of the random alloys for $\beta = 1$, which is the original approximation of the SIM,^{29,31} in general agree quite well with those of the ordered alloys. This is true for v_4 , while v_2 and v_3 are slightly overestimated especially in the NiPt system. For the partially ordered alloys with $\beta = 1$ one finds that v_3 and v_4 differ considerably from the cor-

TABLE I. Two-, three-, and four-site unrelaxed cluster interactions (in K) obtained by calculations for ordered, random, and partially ordered alloys. The Wigner-Seitz radii S are chosen close to the calculated equilibrium value for the ordered phase.

Alloy	S (a.u.)	β	v_2	v_3	v_4
Cu ₃ Au ordered	2.773		6864	503	11
Random		1.0	7714	788	17
Random plus LRO			7722	3504	1097
Random		0.74	6938	671	30
Random plus LRO			6815	687	133
CuAu ordered	2.90		4411	311	-2
Random		1.0	4773	465	20
		0.74	4362	385	21
Au ₃ Cu ordered	3.00		3142	176	-13
Random		1.0	3293	288	26
Random plus LRO			3457	-811	335
Random		0.74	3057	235	26
Random plus LRO			3104	199	3
Ni ₃ Pt ordered	2.7		8390	953	210
Random		1.0	10540	1801	298
Random plus LRO			10533	9007	3186
Random		0.6	8475	1386	267
Random plus LRO			8206	1117	384
NiPt ordered	2.8		5847	694	148
Random		1.0	7113	1254	236
		0.6	5784	946	214
Pt ₃ Ni ordered	2.9		4096	490	96
Random		1.0	4812	831	159
Random plus LRO			5552	-2875	1050
Random		0.6	3996	609	141
Random plus LRO			4259	725	-112

responding values extracted from the random as well as the ordered alloy calculations. Finally, one observes that at $\beta = 0.74$ for Cu-Au and $\beta = 0.6$ for Ni-Pt the cluster interactions of random and partially ordered alloys are consistent with those of the ordered alloys. A measure of the accuracy with which these cluster interactions should agree may be provided by plots of calculated total energies of the kind shown in Fig. 1.

B. Cluster interactions: Dependence on charge transfer

When β is changed from 1 to its optimal value the extracted cluster-interaction parameters will reflect the corresponding change in the electrostatic interactions connected with charge-transfer effects. In the two systems under consideration it turns out that the effective charge transfer $Q_i^A - Q_i^B$ that enters (15) varies almost linearly with concentration and is practically independent of the value of the LRO parameter. Furthermore, $Q_i^A - Q_i^B$ changes little between sublattices and one may therefore define a single effective charge transfer

$$Q_i^A - Q_i^B \equiv \Delta Q = Q_0 + \sigma Q_1, \quad (20)$$

which allows us to estimate the contribution from (15) to the Connolly-Williams interactions. On the basis of the total energies of two pure components and three alloys with compositions corresponding to σ , 0, and $-\sigma$ the contributions to the cluster interactions of a random alloy are found to be

$$\begin{aligned} v_2^r &= \beta \frac{1}{4} (Q_0^2 - Q_1^2) / R_1, \\ v_3^r &= \beta \frac{1}{4} 2Q_0 Q_1 / R_1, \\ v_4^r &= \beta \frac{1}{4} Q_1^2 / R_1. \end{aligned} \quad (21)$$

For random Cu-Au alloys at $R_{WS} = 2.773$ bohrs, Q_0 and Q_1 are 0.432 and 0.031, respectively, and for random Ni-Pt random alloys at $R_{WS} = 2.7$ bohrs they are 0.569 and 0.056, respectively. Therefore, in both systems a change in β has the strongest effect on v_2 , while the effect on v_4 is at least two orders of magnitude smaller. This is in good agreement with the values in Table I.

The contributions from (15) to the cluster interactions in A_3B partially ordered alloys with $\eta = 0, 0.5$, and 0.8 (for AB_3 alloys v_3 has the opposite sign) are found to be

$$v_2^p = 1.75E_Q, \quad v_3^p = 5.25E_Q, \quad v_4^p = 1.76E_Q, \quad (22)$$

where

$$E_Q = \beta \frac{3}{16} \frac{\Delta Q^2}{R_1}. \quad (23)$$

It follows that in this case the contributions to all the cluster interactions beginning with v_2 are of the same order of magnitude.

According to (16) the total energies of the pure components and the random alloys determine mainly the lowest terms of the expansion, i.e., v_0 , v_1 , and v_2 . In Table I it is

seen that v_2 for partially ordered and random alloys are very close. The remaining cluster interaction parameters v_3 and v_4 are determined on the basis of total energies of random and partially ordered alloys at the same concentration. However, by definition these parameters are proportional to the difference in energy of clusters having different configurations. For instance, v_4 is half the difference of the energies of tetrahedra consisting of atoms of opposite types. Now the probability of finding such a cluster in alloys with the same concentration is much smaller than the probability of finding it in alloys with different concentrations and therefore v_3 and v_4 turn out to be strongly dependent on the LRO parameter. This means that the values of v_3 and v_4 obtained on the basis of total energy calculations for partially ordered alloys are very sensitive indicators of the consistency of the total energies calculated within or beyond the single-site approximation. At the same time, one should remember that this consistency may only be qualitative, as explained above, and therefore it does not make sense to determine β by the requirement that the cluster interactions of ordered and partially ordered alloys should equal each other.

IV. HEATS OF FORMATION

In Tables II and III we have collected the measured heats of formation for Cu-Au and Ni-Pt alloys at the stoichiometric compositions together with the values calculated previously by different first-principles methods. The values calculated in the present work are shown in Tables IV and V. In addition, we display selected values in Figs. 2 and 3. From the data in the tables and in the figure one observes that in view of the large uncertainties involved both experimentally and theoretically the calculated heats of formation of the ordered alloys agree well with each other as well as with the experimental data. Similarly, one observes that for the random (CuAu) alloys the calculated heats of formation based on the CWM for ordered alloys agree quite well.

From the tables one also observes that the results of different CPA calculations for random Cu-Au and Ni-Pt alloys differ greatly, depending on how the charge-transfer effects are treated. For example, a complete neglect of (11) and (15) leads to very high, positive values for the heats of formation, as may be seen from our results for random $\text{Cu}_{75}\text{Au}_{25}$ (Table IV) as well as from the results of Ref. 28 for $\text{Ni}_{50}\text{Pt}_{50}$ (Table III). This is to be expected because, according to (15), the contribution to the heat of formation from charge-transfer effects will be negative. In fact, LMTO CPA calculations with $\beta = 1$ lead to substantial reductions in the calculated heats of formation as shown in Tables IV and V. In this respect the results of the KKR CPA calculations by Weinberger *et al.*¹¹ for random Cu-Au alloys are quite unexpected. In spite of the fact that in these calculations charge-transfer effects are completely neglected, i.e., terms of the kind (11) and (15) are ignored, these authors calculate heats of formation that are negative and very close to the experimental data.

TABLE II. Heats of formation of Cu_3Au , CuAu , and Au_3Cu ordered and random alloys (in cal/mol). The acronyms in the table are as follows: ASW is the augmented spherical wave method, FLAPW the full potential linearized augmented plane wave method, KKR the Korringa-Kohn-Rostoker method, and CPA-0 stands for the CPA method with complete neglect of charge-transfer effects both in the potential and the energy. Values in parentheses are read off published figures while numbers in square brackets refer to temperature.

Phase	Expt. ^a	ASW plus CWM ^b	FLAPW plus CWM ^c	FLAPW ^d	LMTO plus CWM ^e	KKR CPA ^f
Cu_3Au ordered	-1682 [298 K]	-1500	-830	-1106		
Random with SRO	-658 [691 K]		-60 ^g		-(250) ^g	
Random	-1059 [720 K]	620	(1070)		(1360)	-(620)
CuAu ordered	-2150 [320 K]	-1608	-1450			
Random with SRO	-1230 [720 K]		-390 ^g		-(60) ^g	
Random	-1150 [693 K]	667	(870), 1567 ^h		(1410)	-(1250)
Au_3Cu ordered	-1136 ⁱ	-784	-610			
Random with SRO	-710 [720 K]		~ 0 ^g		-250 ^g	
Random		471	(410)		(910)	-(720)

^aReference 43.

^bReference 3.

^cReference 4.

^dReference 10.

^eReference 12.

^fReference 11.

^gAt 800 K.

^hReference 9.

ⁱValue obtained from the ordering energy of Ref. 44 and the heat of formation of the random $\text{Au}_{75}\text{Cu}_{25}$ alloy of Ref. 43.

TABLE III. Heats of formation of Ni_3Pt , NiPt , and Pt_3Ni ordered and random alloys (in cal/mol). FLMT0 stands for the full-potential LMTO. Values in parentheses are read off published figures.

Phase	Expt. ^a	FLMT0 plus CWM ^b	LMTO ^b	LMTO plus CWM ^c	LMTO plus CPA ^d
Ni_3Pt ordered		-1975	-2250		
Random with SRO	-1620			-(820) ^e	
Random				(470)	
NiPt ordered		-2727	-2667		-2132 ^f
Random with SRO	-2214	-1700 ^e		-(1400) ^e	
Random				(240)	3323 ^g -2414 ^h
NiPt_3 ordered		-2007	-2102		
Random with SRO	-1500			-(920) ^e	
Random				(~ 0)	

^aReference 45. Interpolated values for $\text{Ni}_{75}\text{Pt}_{25}$ and $\text{Pt}_{75}\text{Ni}_{25}$. The experiments were performed at 298 K on samples quenched from 1473 K. The structures are assumed to be random but no information concerning the structural state is given.

^bReference 15.

^cReference 12.

^dReference 28.

^eAt 1473 K.

^fIncluding combined correction terms and neutral spheres.

^gCPA with complete neglect of charge-transfer effects both in the potential and the energy.

^hCPA using neutral spheres.

TABLE IV. Heats of formation of Cu_3Au , CuAu , and Au_3Cu ordered and random alloys (in cal/mol) calculated in the present work by SIM CPA. For $\beta = 0.74$ the LMTO CWM and the SIM CPA calculations yield identical heats of formation. CPA-0 stands for the CPA method with complete neglect of charge-transfer effects both in the potential and the energy.

Phase	β	Cu_3Au	CuAu	Au_3Cu
Ordered		-1400	-1923	-1293
Random	0.74	1260	1022	457
	1.0	564	246	80
	CPA-0	3317		

In both real Cu-Au and Ni-Pt alloys there are strong short-range-order effects in addition to the effects of local lattice relaxation.^{4,10,12,15} As may be seen from Table II, the calculated heats of formation of random Cu-Au alloys with SRO effects but neglecting lattice relaxation effects are still substantially larger than the corresponding experimental values. In fact, to compare the results of the KKR CPA calculations¹¹ with the experimental data one must correct for SRO and lattice relaxation effects. According to different estimates,^{10,46} such corrections are large and negative and would make the results of Ref. 11 even more negative than the measured heats of formation of the ordered alloys. It would seem that this underestimate of the heats of formation is a fault of the SS CPA. However, this is not substantiated by the present calculations, which show that methods based on the CPA can be made as accurate and reliable as the usual first-principles methods for ordered solids.

V. ORDERING ENERGY AND LATTICE SPACING

Once the optimal value for β has been determined one may use the multisublattice CPA method described in Sec. IIA to calculate the total energy of an alloy as a function of LRO parameter and volume. Thereby one may obtain heats of formation and lattice spacings as functions of the LRO parameter. In Fig. 4 we show the results of such calculations for partially ordered CuAu and NiPt alloys. It is seen that in both alloy systems the heats of formation are almost exact quadratic functions

TABLE V. Heats of formation of Ni_3Pt , NiPt , and Pt_3Ni ordered and random alloys (in cal/mol) calculated in the present work by the SIM CPA. For $\beta = 0.6$ the LMTO CWM and the SIM CPA calculations yield identical heats of formation.

Phase	β	Ni_3Pt	NiPt	Pt_3Ni
Ordered		-2090	-2808	-2861
Random	0.6	1130	446	-180
	1.0	-1440	-1925	-1500

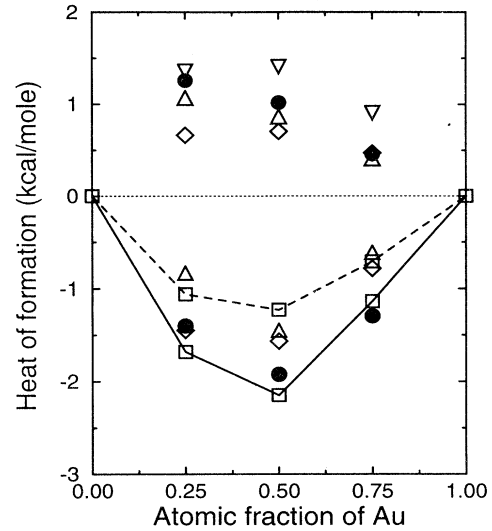


FIG. 2. Experimental and calculated heats of formation for Cu-Au. The negative values are experimental values for ordered and random alloys with SRO and calculated results for ordered alloys. The positive values are calculated results for completely random alloys. The experimental values from Ref. 43 are labeled by open squares connected by a full line for ordered alloys and by open squares connected by a broken line for random alloys with SRO. Filled circles are from the present work, open diamond from Ref. 3, open triangles from Ref. 4, and inverted open triangles from Ref. 12.

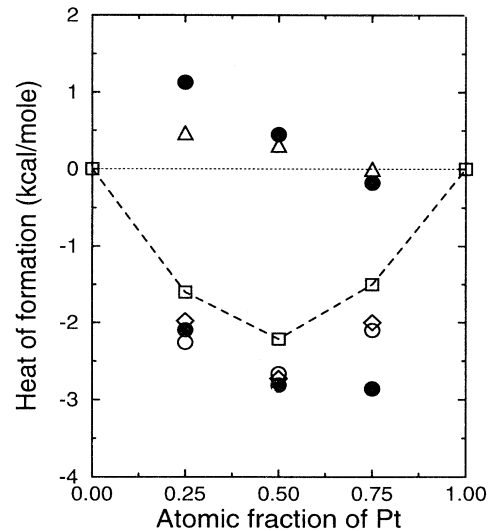


FIG. 3. Experimental and calculated heats of formation for Ni-Pt. The negative values are experimental values for ordered alloys while the positive values are calculated results for completely random alloys. The experimental values for random alloys with SRO from Ref. 45 are labeled by open squares connected by a broken line. Filled circles are from the present work, open diamond are FLMT0 plus CWM results from Ref. 15, open circles are LMTO results from Ref. 15, and open triangles are LMTO CWM results from Ref. 12.

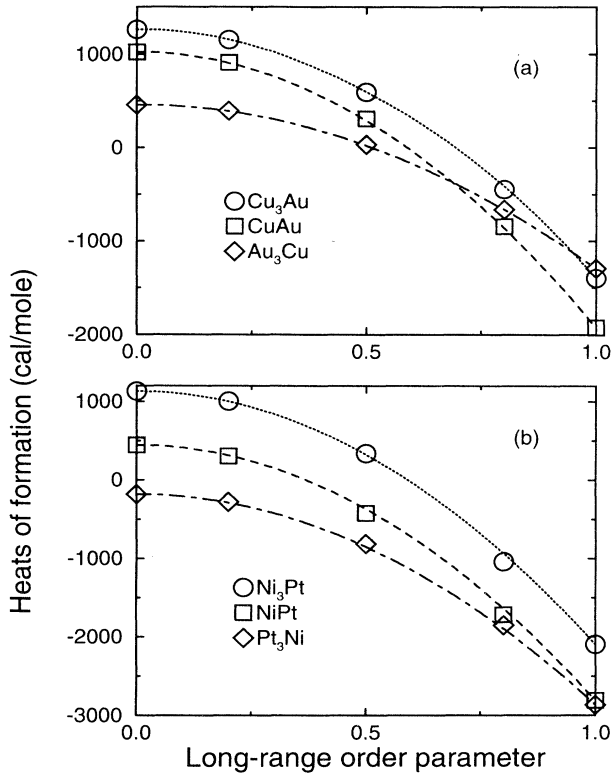


FIG. 4. Heats of formation for partially ordered (a) Cu-Au and (b) Ni-Pt alloys as functions of long-range-order parameter. The calculated values are labeled by circles (Cu_3Au and Ni_3Pt), squares (CuAu and NiPt), and diamonds (Au_3Cu and Pt_3Ni). The curves shown correspond to fits to the quadratic expression (24).

of the LRO parameter and may be written in the form

$$\Delta H(\eta) = \Delta H_r + \eta^2(\Delta H_o - \Delta H_r), \quad (24)$$

where $\Delta H(\eta)$, ΔH_r , and ΔH_o are the heats of formation of partially ordered, random, and ordered alloys, respectively. Similarly, we find that the equilibrium lattice spacings shown in Fig. 5 may be approximated by the quadratic form

$$a(\eta) = a_r - \eta^2(a_r - a_o) = a_r - \eta^2\Delta a, \quad (25)$$

where $a(\eta)$, a_r , and a_o are the equilibrium lattice spacings of partially ordered, random, and ordered alloys, respectively.

The quadratic dependencies may be analyzed in a model based on the CWM cluster expansion (17), which for an A_3B compound and to lowest order in lattice spacing a and LRO parameter η may be written

$$\Delta H(a, \eta) = \frac{9}{8}B_r a_r (a - a_r)^2 - \frac{1}{4}v_2(a_o)\eta^2 - \frac{1}{4} \frac{\partial v_2}{\partial a} \bigg|_{a_r} (a - a_r)\eta^2, \quad (26)$$

where B_r is the bulk modulus of the random alloy. In (26) we have used the observation that the leading cluster

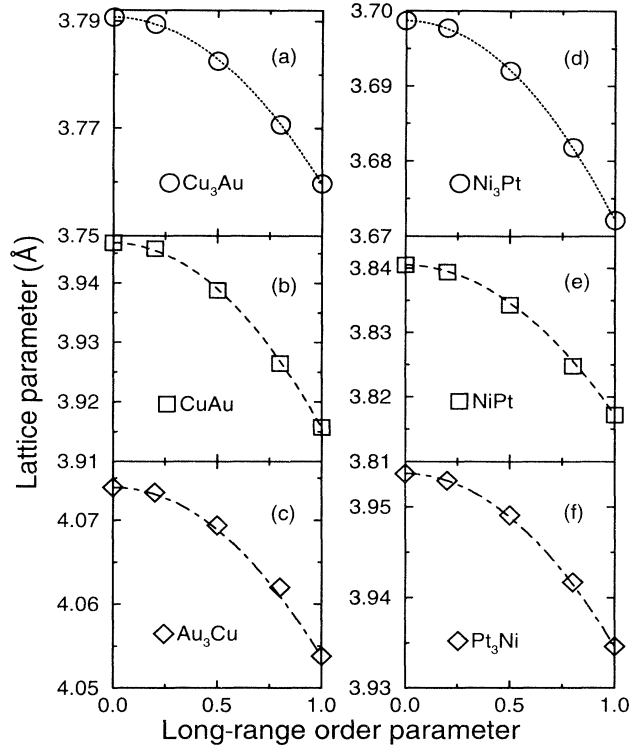


FIG. 5. Equilibrium lattice parameters for partially ordered (a)–(c) Cu-Au and (d)–(f) Ni-Pt alloys. The calculated values are labeled by circles (Cu_3Au and Ni_3Pt), squares (CuAu and NiPt), and diamonds (Au_3Cu and Pt_3Ni). The curves shown correspond to fits to the quadratic expression (24).

interaction v_2 to a good approximation varies linearly with a . If ΔH is minimized with respect to a at fixed η we obtain the quadratic behavior (25) with

$$\Delta a = \frac{\partial v_2 / \partial a|_{a=a_r}}{9B_r a_r}. \quad (27)$$

Furthermore, when this result is inserted into (26) and we keep only the dominating term proportional to v_2 we obtain (24), thereby explaining the quadratic variation of both the heats of formation and the lattice spacing with the LRO parameter η .

One may compare the calculated values for Δa with existing experimental values.⁴⁷ The experimental values are, for Cu_3Au , $3.754 - 3.747 = 0.007$ Å; for CuAu , $3.874 - 3.865 = 0.009$ Å; and for Au_3Cu , $3.983 - 3.980 = 0.003$ Å, while the calculated values are 0.031 Å, 0.031 Å, and 0.02 Å, respectively. In this comparison one should note that the calculations neglect short-range-order effects as well as lattice relaxation effects. Thus one may only expect that the calculated values for Δa are larger than the experimental values, as is indeed the case.

VI. SUMMARY

We have shown that first-principles methods for random alloys based on the single-site coherent-potential ap-

proximation may give an accurate and reliable description of the thermodynamic properties of random metallic alloys. To obtain such a description one must take proper account of charge-transfer effects. For this purpose we have used the screened impurity model based on the assumption that all the charge, which compensates the net charge on an impurity in a metal, is localized in the first coordination shell around the impurity. Since the spatial distribution of this charge is unknown in the single-site approximation, the prefactor β , which is needed in the expression for the electrostatic energy (15), cannot be uniquely defined from theoretical arguments. In the present work the prefactor is chosen such that the binding energies for random alloys calculated by the single-site CPA agree with the corresponding binding energies calculated by the CWM where the latter calculations include charge-transfer effects beyond the single-site approximation. For a given alloy system characterized by

atomic species and crystal structure we find that a single prefactor describes the contribution to the total energy from charge-transfer effects. Furthermore, when an optimal value is found, the Connolly-Williams cluster interactions obtained on the basis of total energy calculations on random alloys in the single-site approximation are consistent with the cluster interactions extracted from total energy calculations on ordered alloys going beyond the single-site approximation.

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